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Bio-/Photo-Chemical Separation and Recovery of Uranium

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Summary

Citric acid forms bidentate, tridentate, binuclear or polynuclear species with transition metals and actinides. Biodegradation of metal citrate complexes is influenced by the type of complex formed with metal ions. While bidentate complexes are readily biodegraded, tridentate, binuclear and polynuclear species are recalcitrant. Likewise certain transition metals and actinides are photochemically active in the presence of organic acids. Although the uranyl citrate complex is not biodegraded, in the presence of visible light it undergoes photochemical oxidation/reduction reactions which result in the precipitation of uranium as $UO_3 \cdot H_2O$. Consequently, we developed a process where uranium is extracted from contaminated soils and wastes by citric acid. The citric-acid extract is subjected to biodegradation to recover the toxic metals, whereas uranyl citrate which is recalcitrant remains in solution. Photochemical degradation of the uranium citrate complex resulted in the precipitation of uranium. Thus the toxic metals and uranium in mixed waste are recovered in separate fractions for recycling or for disposal. The use of naturally-occurring compounds and the combined chemical and microbiological treatment process is more efficient than present methods and should result in considerable savings in cost.

Introduction

Various extraction techniques have been developed to remove uranium from ores, wastes streams and contaminated materials and soils. These include physical methods, such as wet-screening, attrition scrubbing, and chemical methods consisting of treating the material with organic and inorganic acids, salts, bases, and chelating agents. For example, nitric acid, hydrochloric acid, phosphoric acid, sulfuric acid, sodium carbonate, ammonium carbonate, sodium hydroxide, oxalic acid, citric acid, EDTA, and DTPA have been used to extract radionuclide and toxic metals. Many of the inorganic chemicals used are corrosive, which irreparably damages the soil. Furthermore, all chemical extraction methods generate secondary waste streams which create further problems of hazardous waste disposal.

Among the several organic complexing agents used in extracting metals, citric acid appears to be the most preferred because it is a naturally occurring organic complexing agent. It is environmentally friendly, and exhibits relatively consistent removal efficiency. Citric acid forms different types of complexes with the transition metals and actinides, and has been used to extract plutonium from contaminated soils (*18*), to decontaminate components of nuclear reactors, (U.S. Patent Nos. 4,839,1000; 4,729,855; 4,460,500; 4,587,043; 4,537,666; 3,664,870, and 3,103,909), to extract metals and radionuclides such as arsenic, barium, cadmium, cesium cobalt, copper, chromium lead, nickel, zinc, strontium, thorium, and uranium from contaminated soils, wastes, and municipal solid waste incinerator ash (*10*).

Uranium Complexation with Citric acid

Citric acid is a naturally occurring, multidentate ligand which forms stable complexes with various metal ions (*2, 12, 15, 20, 21*). It forms stable complexes with transition metals and actinides and can involve formation of bidentate, tridentate, binuclear, or polynuclear complex species (Figure 1). Calcium, ferric iron and nickel formed bidendate, mononuclear complexes with two carboxylic acid groups of the citric acid molecule. Copper, ferrous iron, cadmium and lead formed tridentate, mononuclear complexes with citric acid involving two carboxylic acid groups and the hydroxyl group. Uranium has been shown to form a predominantly binuclear complex with two uranyl ions and two citric acid molecules involving four carboxylic groups and two hydroxyl groups. However, the proposed basic structure can vary as a result of changes in solution pH (*20*), the ratio of uranium to citrate (*21*), temperature (*2*) and presence of other metals (*7*).

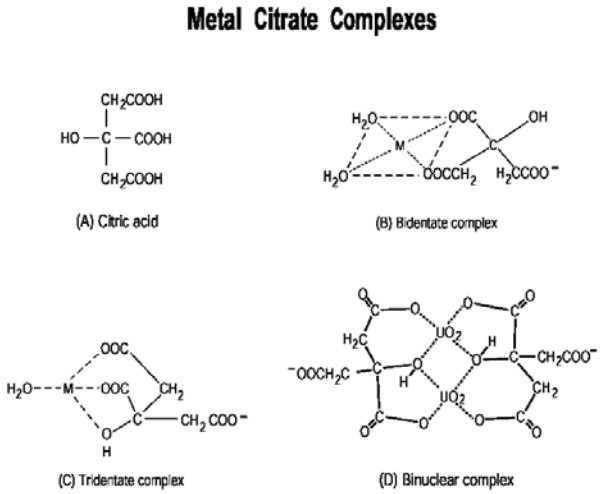

Figure 1. Citric acid, a hydroxytricarboxylic acid forms different types of complexes with metals (*12*).

Biodegradation of Uranyl and Other Metal Citrate Complexes

The type of complex formed plays an important role in determining its biodegradability (*12*) (Figure 2). The rate and extent of biodegradation of several metal-citrate complexes by microorganisms varies. For example, *Pseudomonas pseudoalcaligenes* degraded Mg-citrate at a much lower rate than Ca-, Fe(III)-, and Al(III)-citrate (*17*). Studies with a *Klebsiella sp*. showed that citric acid and Mg-citrate were readily degraded, whereas Cd-, Cu-, and Zn-citrate were resistant (*3*). Both studies also showed that metal toxicity was not responsible for the lack of or the lower rate of degradation of certain metal-citrate complexes but gave no other explanation. Biodegradation studies with *Pseudomonas fluorescens* showed that bidentate complexes of Fe(III)-, Ni-, and Zn-citrate were readily biodegraded, whereas complexes involving the hydroxyl group of citric acid, the tridentate Al-, Cd- and Cu-citrate complexes, and the binuclear U-citrate complex were not (*12, 16*) (Figure 2). The presence of the free hydroxyl group of citric acid is the key determinant in effecting biodegradation of the metal complex. The lack of degradation was not due to their

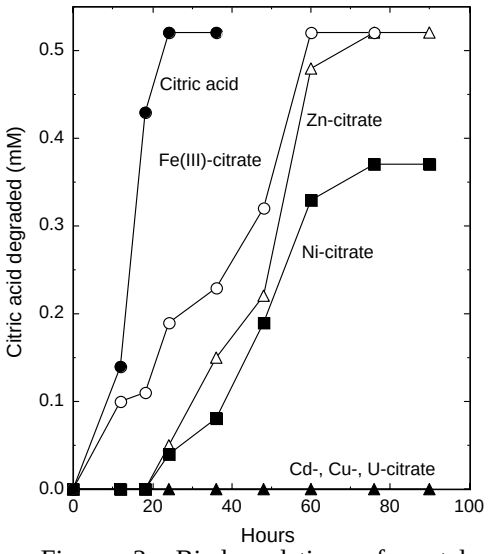

Figure 2. Biodegradation of metal citrates by *Pseudomonas fluorescens* (*12, 16*).

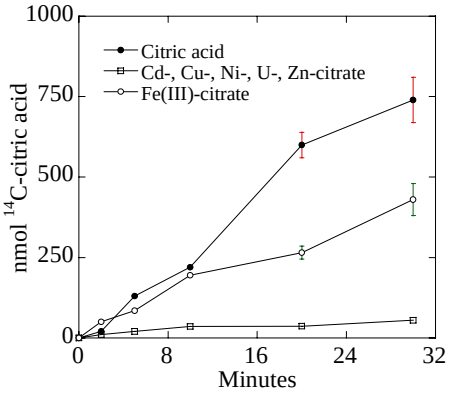

Figure 3. Uptake of ^{14}C-labelled metal-citrate complexes by *P. fluorescens* (*16*)

toxicity, but was limited by the transport and/or metabolism of the complex by the bacteria (*16*) (Figure 3). No relationship was observed between biodegradability and stability of the complexes. The tridentate Fe(II)-citrate complex, although recalcitrant, was readily biodegraded after oxidation and hydrolysis to the bidentate Fe(III)-citrate form, denoting a structure-function relationship in the metabolism of the complex (*13*). Biodegradation of Fe(III)-citrate complex resulted in the formation of carbon dioxide and ferrihydrite. Uranyl-citrate however, is not biodegraded and remains in solution relatively in a pure form which can be further processed by ion exchange without fouling by other metals or photodegradation.

Photodegradation of Uranyl Citrate

Uranyl ion is photochemically active in the presence of organic acids, and up on exposure to visible light, the uranyl citrate complex undergoes photochemical oxidation/reduction reactions. Adams and Smith (*1*) observed complete photochemical reduction of uranyl ion to U(IV) in the absence of oxygen, but only partial reduction in the presence of oxygen, resulting in the formation of an unidentified soluble polymeric from of uranium. Subsequently, Ohyoshi and Ueno (*19*) reported the oxidation of citric acid to acetone and carbon dioxide at acidic pH through an unidentified ketocarboxylic acid intermediate, but they did not investigate the fate of uranium.

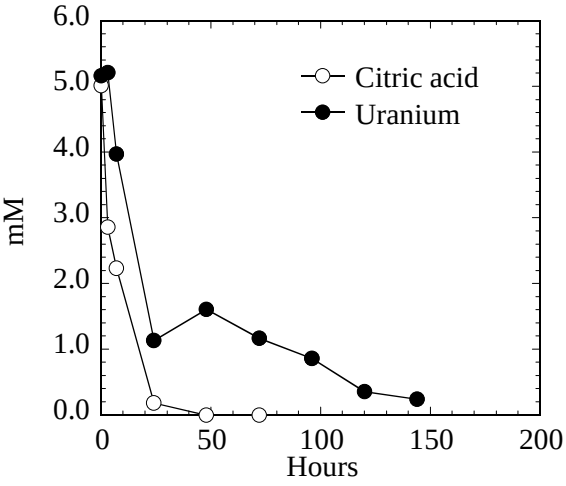

Figure 4. Photodegradation of U-citrate complex (*4*).

Dodge and Francis (*4*, *6*) reported that exposure of uranyl citrate complex to visible light (400 to 700 nm) showed photodegradation of citric acid to acetic acid and carbon dioxide, with precipitation of uranium as uranium trioxide ($UO_3 \cdot 2H_2O$) (Figure 4). The reaction proceeds by a complex step-wise process. Uranium is reduced to U(IV) from U(VI) by a 2-electron transfer from citrate with production of a mononuclear U(IV)-citrate complex, acetoacetate, uranyl ion, and CO_2 (Reaction 1). The acetoacetate is unstable in the presence of oxygen and undergoes intramolecular rearrangement to form acetone and acetic acid (Reaction 2). A photochemically generated H atom combines with O_2 to form a hydroperoxy radical which oxidizes U(IV)-citrate to U(V)-citrate complex (Reaction 3). The weak pentavalent complex dissociates (Reaction 4) and U(V) undergoes disproportionation reaction to U(IV) and U(VI) ions (Reaction 5). The U(VI) precipitates from solution as the mineral schoepite (Reaction 6). Overall net consumption of H^+ ions results in pH increase from 3.5 to 5.1.

$$[(UO_2)_2(Hcit)_2]^{2-} + 2H^+ \xrightarrow{h\nu} [HcitU(OH)_2)]^- + UO_2^{2+} + \underset{\displaystyle CH_2COO^-}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C=O}}}} + CO_2 + H_2O \quad (1)$$

$$2\ \underset{\displaystyle CH_2COO^-}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C=O}}}} + H_2O \rightarrow 2\ CH_3COO^- + \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C=O}}}} + CO_2 \quad (2)$$

$$[HcitU(OH)_2)]^- \xrightarrow{h\nu} [HcitUO(OH)]^- + H + O_2 \xrightarrow{\cdot O_2H} [HcitUO_2]^{2-} + H^+ \quad (3)$$

$$[HcitUO_2]^{2-} \rightarrow UO_2^+ + Hcit^{3-} \quad (4)$$

$$2UO_2^+ + 2H^+ \rightarrow UO_2^{2+} + UO^{2+} + H_2O \quad (5)$$

$$UO_2^{2+} + 3H_2O + \rightarrow UO_3{\cdot}2H_2O\ (ppt.) + 2H^+ \quad (6)$$

The initial pH and the presence of oxygen affected the rate and extent of photochemical degradation of the complex, the formation of intermediate organic degradation products, and the uranium speciation (*6*). Under aerobic conditions at pH 3.5, acetic, acetoacetic, 3-oxoglutaric, and malonic acids and acetone were detected; at pH 6.0, 3-oxoglutaric and acetic acids were present. The uranyl U(VI) ion was reduced to uranous U(IV) ion and was subsequently reoxidized to the hexavalent from and precipitated out of solution as uranium trioxide. The precipitate was identified as meta-schoepite ($UO_3{\cdot}2H_2O$), a form of uranium trioxide, by X-ray diffraction analysis (XRD). Extended X-ray absorption fine structure spectroscopy (EXAFS) (Figure 5) at the National Synchrotron Light Source (NSLS) confirmed the presence of a U-U interaction at 4.13 Å due to the polymerization of the precipitate. In addition the precipitate has a first shell consisting of 2 O atoms at 1.79 Å, confirming the presence of the double bonded axial oxygens surrounding the hexavalent urnaium and a split second shell containing 1.5 U-O interactions at 2.24 Å and 2.5 O interactions at 2.47 Å, which are typical atomic parameters for a uranium oxide precipitate. The precipitate was quite insoluble at the near neutral pH, and was somewhat soluble in acidic pH (<3.5). Under anaerobic conditions, the uranyl citrate complex showed only partial (57%) degradation, and uranium was present in the reduced form as U(IV). Excess citric acid retarded the precipitation of uranium.

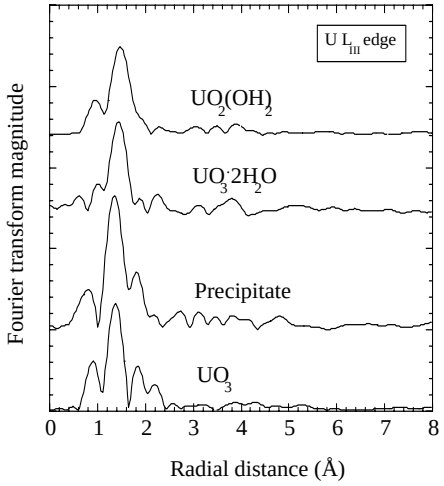

Figure 5. EXAFS spectra of uranium trioxide precipitate from photodegradation of U-citrate complex (*6*).

Extraction and Recovery of Uranium

The presence of radionuclides and toxic metals in wastes, soils, sediments, and materials is a major environmental concern. Unlike organic contaminants, the metals cannot be destroyed, but must either be converted to a stable form or removed. A comprehensive process has been developed for the removal and recovery of radionuclides and toxic metals from contaminated soils, sludges, incinerator ash, and wastes (U.S. Patent No. 5,292,456). The process extracts metal contaminants from soil/wastes and then converts them to a concentrated and stable form. The reduction in volume and mass of the waste renders it amenable for recovery, recycling or disposal.

Process Description. The overall process consists of three steps: extraction, biodegradation, and photodegradation (Figure 6). Citric acid, a naturally occurring organic complexing agent, is used to extract metals and radionuclides from contaminated soils and wastes by formation of different types of complexes such as bidentate, tridentate, binuclear and polynuclear species. The extract containing radionuclides and metals is subjected to biodegradation resulting in the bioprecipitation of metals such as Ba, Cd, Cr, Ni, Zn, and radionuclides Co, Sr, and Th which are recovered in a concentrated form. Uranium forms a binuclear complex with citric acid which is not biodegraded and is present in solution. The supernatant containing the uranium in solution after biodegradation of the extract is separated and upon exposure to light, undergoes rapid photodegradation resulting in the precipitation of uranium as a stable oxide ($UO_3 \cdot 2H_2O$). Uranium is recovered in a concentrated form after photodegradation for recycle or disposal.

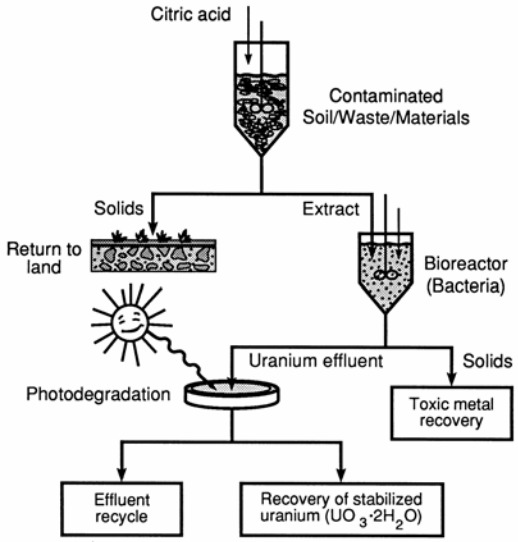

Figure 6. Schematic of citric acid treatment process (*10, 11*).

Key Experimental Results. The Citric Acid Process has been successfully tested to treat uranium and toxic metals contaminated soils from Fernald (FERMCO), and Ashtabula (RMI) sites in Ohio, and sludge from uranium processing plant at Y-12, Oak Ridge, TN. Using single step batch extractions, 70 - 99% of the uranium has been effectively removed from the sludge and soil samples (*8-11*). Biodegradation and photodegradation treatments of the extract resulted in >99% removal and recovery of the extracted uranium.

The Citric Acid Process has also been used to remove lead, cadmium and other toxic metals from municipal solid waste incinerator ash. Bench-scale and pilot studies in has shown that >95% lead was removed from the ash. The treated ash is suitable for reuse as road base and construction aggregate.

Economics and Market Potential. The Citric Acid Process has significant potential for commercialization because (i) it can be applied to a variety of materials and waste forms; (ii) mixed waste is separated into radioactive and hazardous waste; (iii) uranium is separated from the toxic metals and recovered for recycling or disposal; (iv) it does not generate secondary waste streams; (v) it causes little damage to soil; and (vi) environmentally and economically important metals are removed in a concentrated form. The use of combined chemical,

photochemical, and microbiological treatments of contaminated materials will be more efficient than present methods and result in considerable savings in clean-up and disposal costs.

Acknowledgements

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